REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
12-05-2014	Conference Proceeding (refereed)	

4. TITLE AND SUBTITLE
Corrosion Susceptibility of AA5083-H116 in Biologically Active Atmospheric Marine Environments

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
0601153N

6. AUTHOR(S)
J.S. Lee, R.I. Ray, B.J. Little and W.C. Neil

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
73-4635-03-5

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Naval Research Laboratory
Oceanography Division
Stennis Space Center, MS 39529-5004

8. PERFORMING ORGANIZATION REPORT NUMBER
NRL/PP/7330--13-1878

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
One Liberty Center
875 North Randolph Street, Suite 1425
Arlington, VA 22203-1995

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Aluminum alloy (AA) 5083-H116 was exposed to laboratory marine atmospheres with and without fungi. AA5083-Hl16 coupons were half covered with potato dextrose agar (PDA), a fungal growth media; the remaining coupon areas were left bare and fully exposed to the marine atmosphere. Fungal mycelia were inoculated into the PDA and grew over the entire coupon surface during the 90-day exposure. Overlaid with PDA, AA5083-H116 exhibited shallow crystallographic etching and grain boundary attack. Fungi increased the likelihood and severity of pitting corrosion when compared with abiotic controls. Fungal mycelia were associated with trenching and intergranular pits on the bare surfaces. Al-Si-Mg particles were associated with small (10 J..lm) pits over the entire coupon surface, regardless of exposure condition.

15. SUBJECT TERMS
5083, fungi, atmospheric corrosion, marine

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jason Lee
Unclassified	Unclassified	Unclassified	UU	11	19b. TELEPHONE NUMBER *(Include area code)* (228) 688-4494

Paper No.
3976

CORROSION 2014
Collaborate. Educate. Innovate. Mitigate.
March 9-13, 2014 • Henry B. Gonzalez Convention Center • San Antonio, Texas, U.S.A.

CORROSION SUSCEPTIBILITY OF AA5083-H116 IN BIOLOGICALLY ACTIVE ATMOSPHERIC MARINE ENVIRONMENTS

J. S. Lee, R. I. Ray and B. J. Little
Codes 7332/7303
Naval Research Laboratory, Stennis Space Center, MS, USA, 39529

W. C. Neil
Defence Science and Technology Organisation, Fishermans Bend, VIC, Australia 3207

ABSTRACT

Aluminum alloy (AA) 5083-H116 was exposed to laboratory marine atmospheres with and without fungi. AA5083-H116 coupons were half covered with potato dextrose agar (PDA), a fungal growth media; the remaining coupon areas were left bare and fully exposed to the marine atmosphere. Fungal mycelia were inoculated into the PDA and grew over the entire coupon surface during the 90-day exposure. Overlaid with PDA, AA5083-H116 exhibited shallow crystallographic etching and grain boundary attack. Fungi increased the likelihood and severity of pitting corrosion when compared with abiotic controls. Fungal mycelia were associated with trenching and intergranular pits on the bare surfaces. Al-Si-Mg particles were associated with small (10 μm) pits over the entire coupon surface, regardless of exposure condition.

Key words: aluminum 5083, fungi, atmospheric corrosion, marine

INTRODUCTION

Future ship designs and modernization of existing platforms rely on lightweight aluminum. Aluminum 5XXX series alloys, with magnesium (Mg) as the primary alloying element, have garnered increased attention with their expanded use in Naval vessels. Recent research efforts have focused on the sensitization of these alloys.[1,2] Sensitization results from the segregation of Mg to grain boundaries, forming the highly anodic β-phase.[3-6] Aluminum alloy (AA)5083 (UNS A95083) has received the vast majority of attention specifically in regards to intergranular corrosion due to sensitization.[5,7-10] Mizuno and Kelly[7,8] examined the intergranular corrosion behavior of AA5083-H131 during galvanic coupling to steel. The authors showed that penetration depth in AA5083-H131 was particularly correlated to degree of sensitization (DoS) as measured by the standardized nitric acid test ASTM G67.[11] Fatigue and stress corrosion cracking behaviors of sensitized AA5083 have also been evaluated.[12,13] Pitting of AA5083 under immersed seawater conditions has been

examined, but to a lesser extent than the sensitization studies.[14-16] However, little consideration has been given to the impact of naturally occurring marine environments on the predicted lifetime of AA5083. Specifically, microbiological effects on the corrosion properties of AA5083 have not been demonstrated. In the present study, laboratory tests were designed to answer the following questions related to marine corrosion: 1) Can microorganisms survive/grow on AA5083 surfaces in marine conditions; 2) Can colonization of microorganisms on AA5083 initiate and sustain localized corrosion on boldly exposed surfaces?

METHODS AND MATERIALS

Coupons of as-received AA5083-H116 (1.59 cm dia. x 0.16 cm thick) were mounted in EpoThin ™ epoxy (Buehler, Lake Bluff, IL) and polished to 1 μm finish. Mounted coupons were placed face up in square (20 cm x 20 cm x 6 cm) plastic containers. Three containers, lids and two coupons per container were washed with iso-propyl alcohol and air-dried. Difco™ potato dextrose agar (PDA) was prepared according to manufacturer instructions and poured into sterile plastic petri dishes to a depth of 1 mm. After solidification, 1.0 cm x 1.5 cm PDA sections were removed and placed on the mounted coupons covering one half of the AA5083-H116 surface (Figure 1). Care was taken to prevent unintended contamination of the PDA by airborne microorganisms by keeping the lids on the containers when not in use. Fungal species *Aspergillus niger* and *Penicillium oxalicum* were grown on separate PDA plates inoculated from frozen stock specimens. These fungi are known to deteriorate coated and bare A2XXX series aluminum alloys.[17-21] Both fungi produced mycelia that were transferred to the PDA sections by inoculating loops. One container contained only *A. niger* while the second contained only *P. oxalicum*; the third container was not inoculated with fungi and served as a control. An aerosol of sterile 3.5% NaCl solution was spayed into each container. Salt loading was not measured. A petri dish filled with sterile 3.5% NaCl was placed in each of the three containers to maintain humidity. The containers were stored in a dark room at 24 °C for 90 days.

After exposure, coupons were photographed, sonicated in soap and water, and acid cleaned in boiling phosphoric acid with dissolved chromium trioxide according to ASTM G1 Designation C.1.1.[22] Corrosion morphology was examined by scanning electron microscopy.

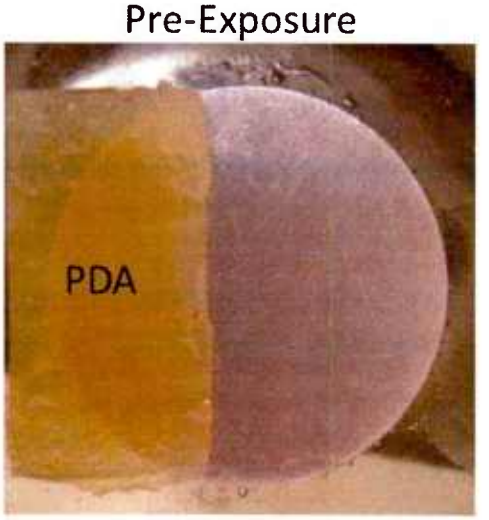

Figure 1. Epoxy mounted AA5083-H116 (1.58 cm dia.) with 1 mm thick potato dextrose agar overlay prior to exposure.

RESULTS & DISCUSSION

Figure 2 shows the representative macroscopic appearance of AA5083-H116 after 90-day exposure to simulated marine atmospheres with and without fungi. Water droplets were visible on all metal and epoxy surfaces after 90 days confirming sufficient humidity was achieved to maintain deliquescence of deposited salt films. After the 90-day exposure, PDA in the control exposure was intact with some shrinkage. Fungal sterility was maintained as evidenced by the lack of observable fungal mycelia or spores in the control PDA. Dark orange spots inside the control PDA corresponded to areas of shallow attack of the AA5083-H116 surface (Figure 3). Prior to solidification, PDA has a pH of 3.5, and has been shown to be corrosive to aluminum 2XXX series alloys.[21] Fungal mycelia were observed on coupons exposed to either *A. niger* or *P. oxalicum*. Mycleia had grown out of the PDA and had colonized the originally bare AA5083-H116 surfaces. PDA was nearly fully digested when exposed to either fungal species. Spore formation was observed at the initial site of PDA overlay. *A. niger* produced dark brown spores while *P. oxalicum* produced a fuzzy olive green spore mat.

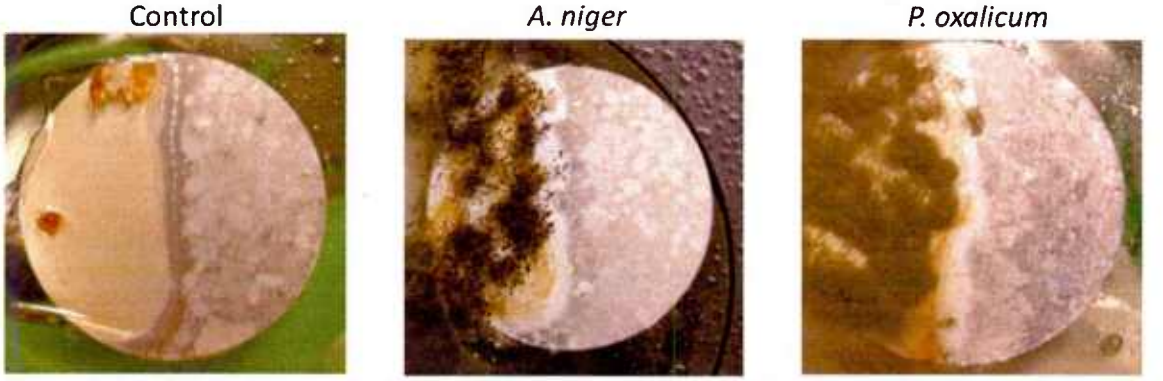

Figure 2. AA5083-H116 coupons after 90-day exposure in marine atmosphere without fungi (control), with *A. niger* and *P. oxalicum*. Fungal myclelium were translucent white in color while spores were brown (*A. niger*) or olive green (*P. oxalicum*). Coupons were 1.59 cm in dia.

Figures 3 and 4 show corrosion morphologies of the control exposure associated with the PDA-covered and bare sides, respectively. Under the PDA (Figure 3), AA5083-H116 was shallowly attacked (20 μm depth) in localized areas. The attack was crystallographic with clearly observable facets. Areas away from the attack had small (10 μm) pits with Al-Si-Mg particles at the bottom. These small particle-associated pits were detected in all exposure conditions, with and without PDA-overlay or fungi. Al-Fe-Mg-Mn-Si particles were also detected. Bare AA5083-H116 (Figure 4) exposed to the marine atmosphere had circular areas, which appeared darker in the SEM, that were covered with Al-Fe-Mg-Mn-Si particles. Circular attack patterns (~30 μm dia.) were associated with water droplets and NaCl crystals.

Figures 5 and 6 show the corrosion morphologies of the exposure with *A. niger* associated with the PDA-covered and bare sides, respectively. Under the PDA (Figure 5), preferential attack of the grain boundaries was observed. In each replicate, multiple isolated pits were detetced under the PDA overlays. Pits had a crystallographic morphology but were deeper (200 μm) than the shallow attack observed in the control exposure. Bare AA5083-H116 (Figure 6) exposed to the marine atmosphere with *A. niger* had circular attack patterns associated with water droplets and NaCl crystals. Surface regions associated with mycelia exhibited dark, long, thin, branched shapes. Pitting was also observed on the bare surface adjacent to the PDA. Pits had ruptured covers and the pitting morphology was intergranular with small regions of crystallographic attack.

Figures 7 and 8 show the corrosion morphologies of the exposure with *P. oxalicum* associated with the PDA covered and bare sides, respectively. Under the PDA (Figure 7), preferential attack of the grain boundaries was observed. Shallow isolated pits were observed under

the PDA overlays. Pits had a crystallographic morphology and were intermediate in depth (40 μm) compared to the control and *A. niger* exposures. Bare AA5083-H116 (Figure 8) exposed to the marine atmosphere with *P. oxalicum* had circular attack patterns associated with water droplets and salt crystals. Trenches were associated with mycelia. Trenches were shallow (<5 μm) and were not crystallographic, but rather had small circular 1 μm pits at the trench bottom. Extensive pitting with intergranular corrosion morphology was also observed in association with *P. oxalicum* mycelia.

Comparison of corrosion morphology as a function of exposure condition demonstrated noticeable trends. AA5083-H116 exposed under PDA resulted in crystallographic pitting with or without fungi present. Fungi increased the depth of crystallographic attack and resulted in preferential grain boundary dissolution. Exposure of bare AA5083-H116 to humid marine atmosphere resulted in circular attack patterns (30 μm dia.) presumably due to water droplet formation and elevated NaCl concentration. In the presence of fungi, intergranular pitting was observed. In addition, trenches with small (1 μm dia.) pits were associated with fungal mycelia. Pits (10 μm dia.) with Al-Si-Mg particles at the bottom were observed over all AA5083-H116 surfaces, regardless of exposure condition.

These experiments represent the first noted microbiologically influenced corrosion (MIC) of AA5083-H116. The results presented here are the first phase of a larger examination regarding MIC of 5XXX aluminum alloys and should be considered qualitative. Continued examination of these exposure specimens is ongoing and further discussion of the results will be detailed in subsequent publications.

CONCLUSIONS

AA5083-H116 was exposed to simulated laboratory marine atmospheres with and without fungi. Observations suggest AA5083-H116 is resistant to significant attack in salt atmospheres; however, the presence of fungi increases the likelihood of pitting. Small pits (10 μm) were associated with Al-Si-Mg particles for all exposures in both bare and PDA-covered surfaces. Crystallographic attack was observed in all exposures conditions under the PDA overlay. In the presence of *A. niger*, pits under the PDA were significantly deeper and more numerous compared with the other exposures. Mycelia from *A. niger* and *P. oxalicum* were associated with trenching and intergranular pits on the bare surfaces. Crystallographic pitting was observed in control exposures only when covered by PDA.

ACKNOWLEDGEMENTS

This work was supported by NRL Base funding. NRL Publication NRL/PP/7330—13-1878.

REFERENCES

1. L. Tan, T. R. Allen, "Effect of thermomechanical treatment on the corrosion of AA5083," Corrosion Science 52, 2 (2010) p. 548-554.
2. N. Birbilis, R. Zhang, M. L. C. Lim, R. K. Gupta, C. H. J. Davies, S. P. Lynch, R. G. Kelly, J. R. Scully, "Quantification of Sensitization in AA5083-H131 via Imaging Ga-Embrittled Fracture Surfaces," Corrosion 69, 4 (2013) p. 396-402.
3. D. H. Choi, B. W. Ahn, D. J. Quesnel, S. B. Jung, "Behavior of beta phase (Al3Mg2) in AA 5083 during friction stir welding," Intermetallics 35 (2013) p. 120-127.
4. R. Goswami, G. Spanos, P. S. Pao, R. L. Holtz, "Precipitation behavior of the beta phase in Al-5083," Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing 527, 4-5 (2010) p. 1089-1095.

5. Y. K. Yang, T. Allen, "Direct visualization of beta phase causing intergranular forms of corrosion in Al-Mg alloys," Materials Characterization 80 (2013) p. 76-85.
6. Y. K. Zhu, D. A. Cullen, S. Kar, M. L. Free, L. F. Allard, "Evaluation of Al3Mg2 Precipitates and Mn-Rich Phase in Aluminum-Magnesium Alloy Based on Scanning Transmission Electron Microscopy Imaging," Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science 43A, 13 (2012) p. 4933-4939.
7. D. Mizuno, R. G. Kelly, "Galvanically Induced Intergranular Corrosion of AA5083-H131 Under Atmospheric Exposure Conditions: Part 1-Experimental Characterization," Corrosion 69, 6 (2013) p. 580-592.
8. D. Mizuno, R. G. Kelly, "Galvanically Induced Intergranular Corrosion of AA5083-H131 Under Atmospheric Exposure Conditions: Part 2-Modeling of the Damage Distribution," Corrosion 69, 7 (2013) p. 681-692.
9. M. L. C. Lim, J. R. Scully, R. G. Kelly, "Intergranular Corrosion Penetration in an Al-Mg Alloy as a Function of Electrochemical and Metallurgical Conditions," Corrosion 69, 1 (2013) p. 35-47.
10. S. Jain, M. L. C. Lim, J. L. Hudson, J. R. Scully, "Spreading of intergranular corrosion on the surface of sensitized Al-4.4Mg alloys: A general finding," Corrosion Science 59 (2012) p. 136-147.
11. ASTM Standard G67-04, "Standard test method for determining the susceptibility to intergranular corrosion of 5XXX series aluminum alloys by mass loss after exposure to nitroc acid (NAMLT Test)," ASTM Hanbook 3.02 Corrosion of Metals; Wear and Erosion. ASTM Hanbook 3.02 Corrosion of Metals; Wear and Erosion (ASTM International: West Conshohocken, PA, 2004).
12. R. Goswami, G. Spanos, P. S. Pao, R. L. Holtz, "Microstructural Evolution and Stress Corrosion Cracking Behavior of Al-5083," Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science 42A, 2 (2011) p. 348-355.
13. R. L. Holtz, P. S. Pao, R. A. Bayles, T. M. Longazel, R. Goswami, "Corrosion-Fatigue Behavior of Aluminum Alloy 5083-H131 Sensitized at 448 K (175 degrees C)," Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science 43A, 8 (2012) p. 2839-2849.
14. N. Dolic, J. Malina, A. B. Hadzipasic, "Pit Nucleation on as-Cast Aluminiuim Alloy Aw-5083 in 0.01m Nacl," Journal of Mining and Metallurgy Section B-Metallurgy 47, 1 (2011) p. 79-87.
15. M. Elboujdaini, E. Ghali, A. Galibois, "Pitting Corrosion of the Aluminum-Alloys 5083-H321 and 6061-T651," Journal of Applied Electrochemistry 18, 2 (1988) p. 257-267.
16. H. Ezuber, A. El-Houd, F. El-Shawesh, "A study on the corrosion behavior of aluminum alloys in seawater," Materials & Design 29, 4 (2008) p. 801-805.
17. D. M. Lavoie, B. J. Little, R. I. Ray, K. R. Hart, P. A. Wagner, "Microfungal degradation of polyurethane paint and corrosion of aluminum alloy in military helicopters," CORROSION / 97, Paper no. 218 (Houston, TX: NACE International, 1997).
18. B. Little, P. Wagner, R. Ray, "Fungal degradation of military assets," 1997 Tri-Service Conference on Corrosion. II. (Carderock Division: Naval Surface Warfare Center, 1997), p. 10.51-10.62.
19. B. J. Little, R. K. Pope, R. I. Ray, "An evaluation of fungal-influenced corrosion of aircraft operating in marine tropical environments," in Marine Corrosion in Tropical Environments, , Vol. STP 1399, eds. S. W. Dean, H.-D. Delgadillo and J. B. Bushman (West Conshohocken, PA: ASTM, 2000), p. 257-269.
20. J. S. Lee, B. J. Little, R. I. Ray, "Microbiologically influenced corrosion in military systems," in ASM Handbook, Vol 13C Corrosion: Environments and Industries, eds. S. D. Cramer and B. S. Covino (Materials Park, OH: ASM International, 2006), p. 211-219.
21. J. T. Stropki, J. L. Tankersley, D. P. Lorch, "Evaluate antimicrobial compounds and their effects on microbially influenced corrosion (MIC)," Final Report, TCN 11-088: Battele Memorial Institute, 2012).
22. ASTM Standard G1-03, "Standard practice for preparing, cleaning, and evaluating corrosion test specimens," ASTM Hanbook 3.02 Corrosion of Metals; Wear and Erosion. ASTM Hanbook 3.02 Corrosion of Metals; Wear and Erosion (ASTM International: West Conshohocken, PA, 2003).

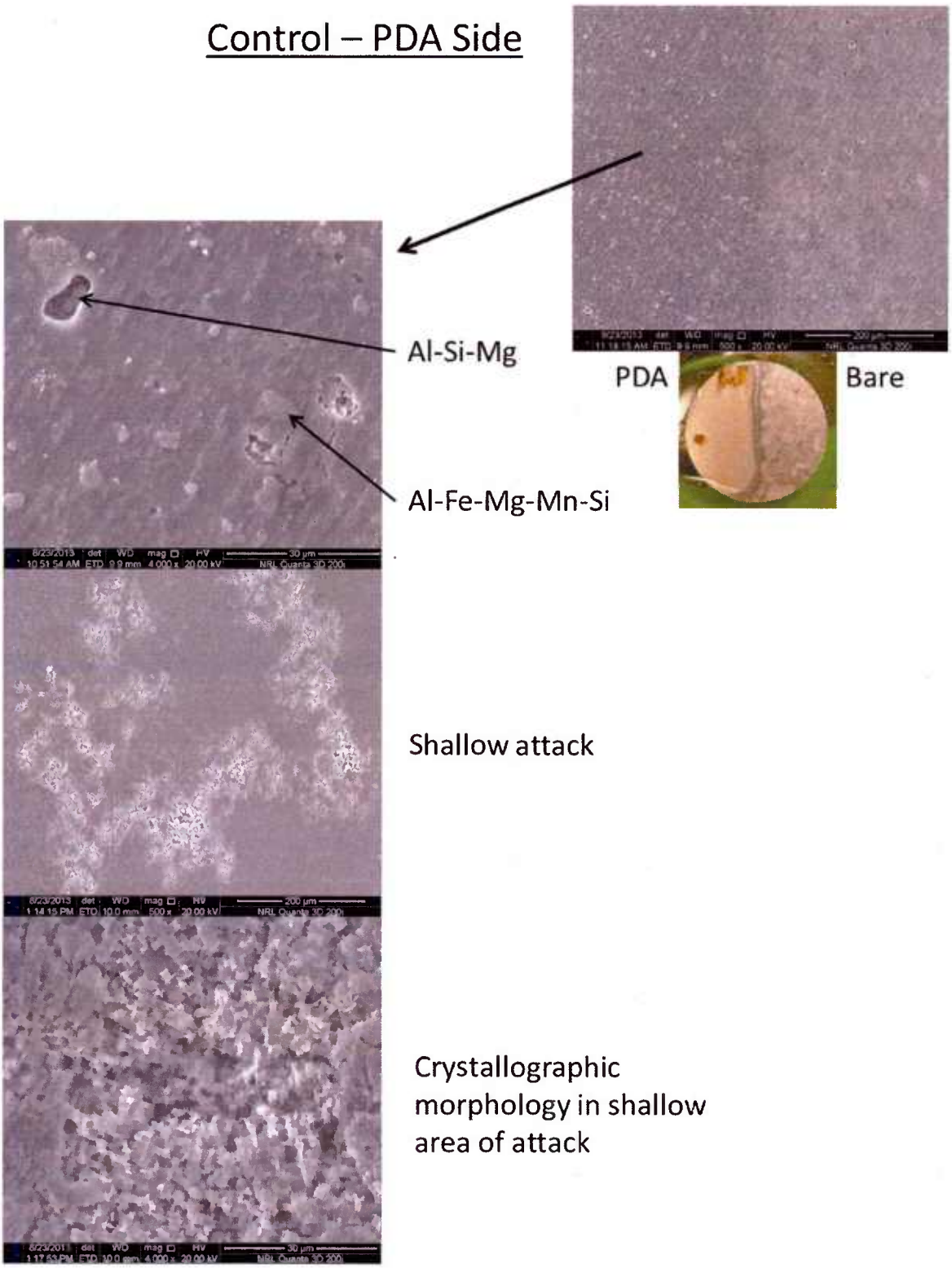

Figure 3. AA5083-H116 surface under PDA after 90-day exposure in marine atmosphere without fungi (control).

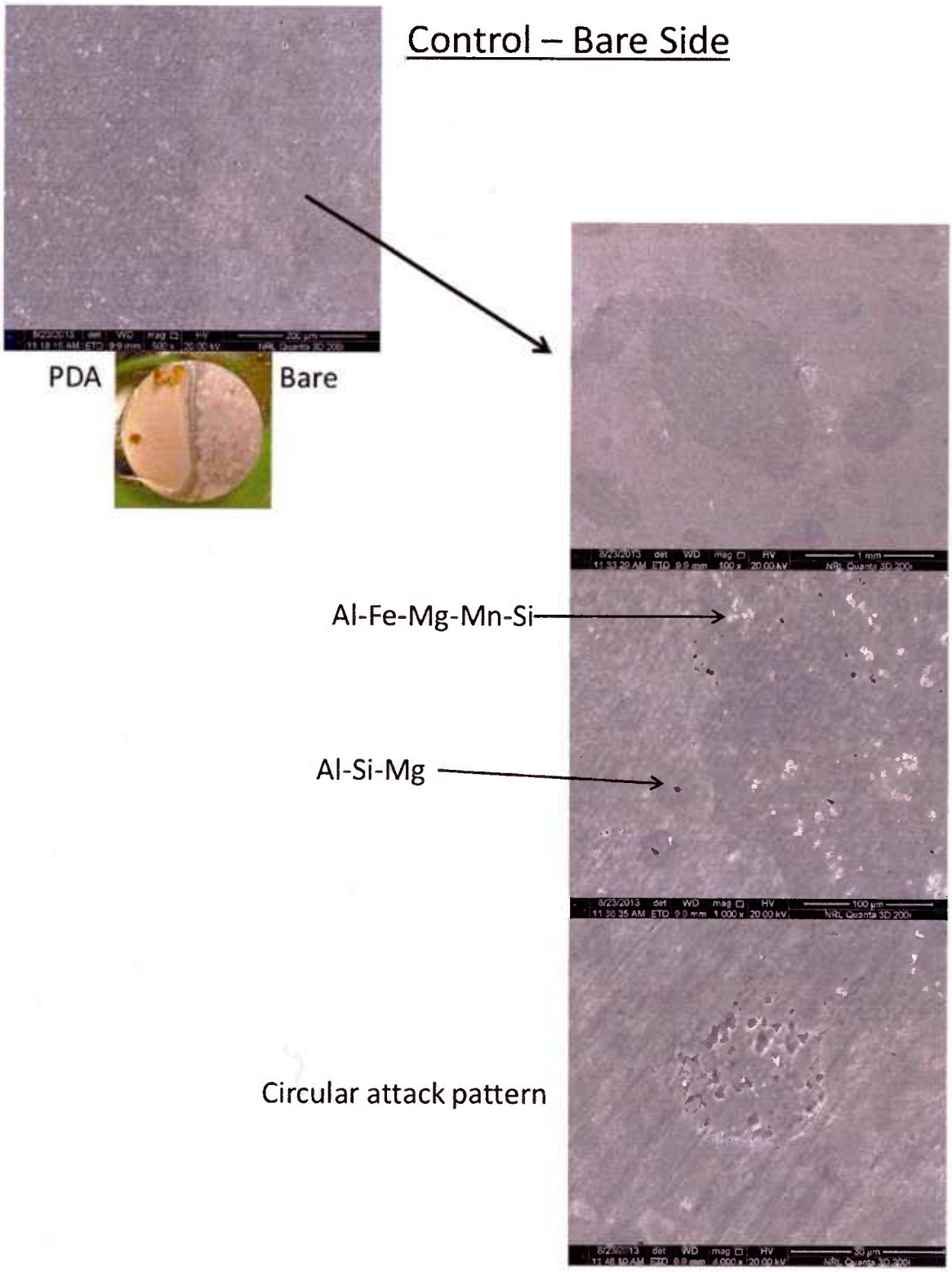

Figure 4. Bare AA5083-H116 coupons adjacent to PDA overlay after 90-day exposure in marine atmosphere without fungi (control).

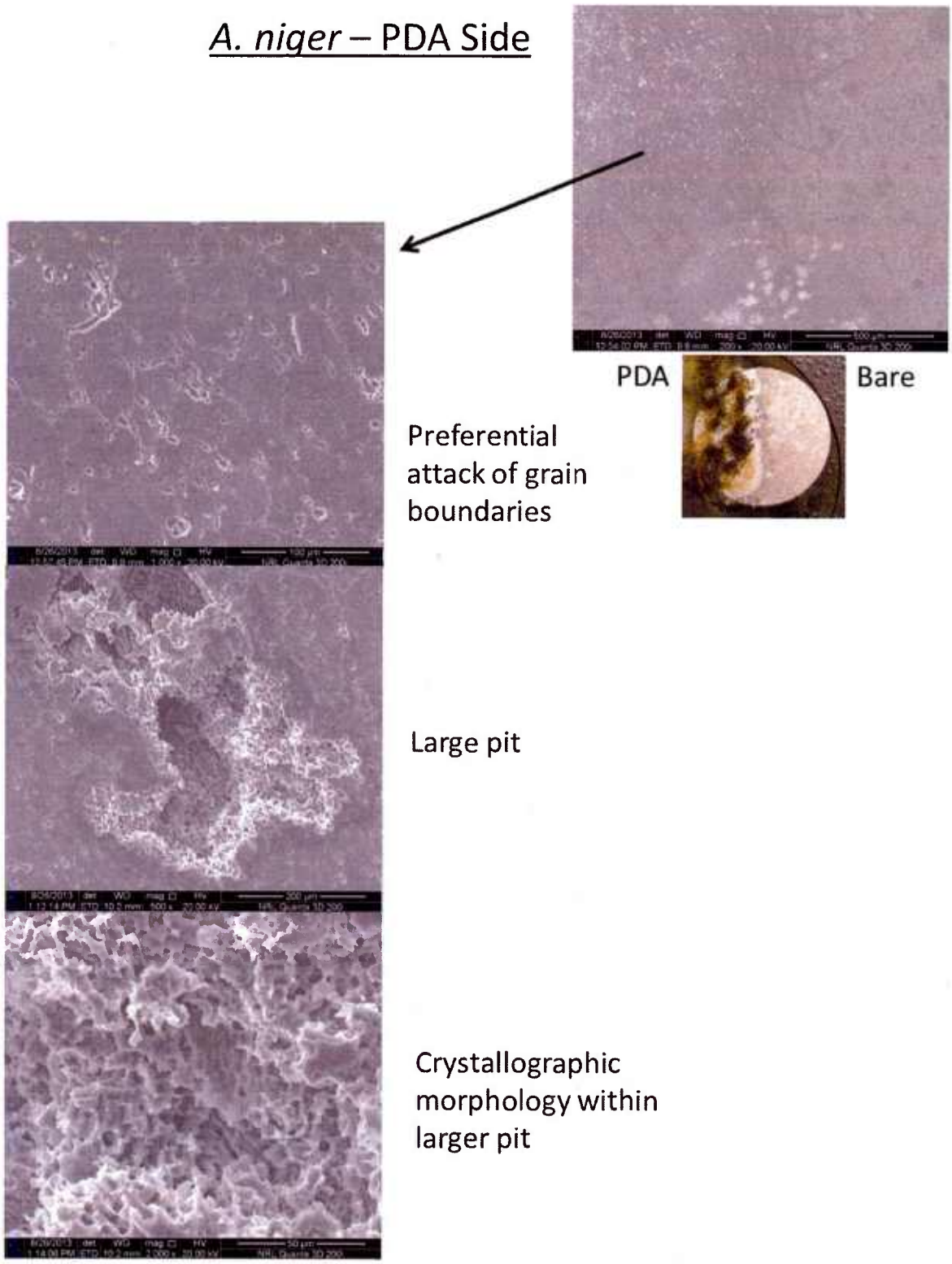

Figure 5. AA5083-H116 surface under PDA after 90-day exposure in marine atmosphere with *A. niger*.

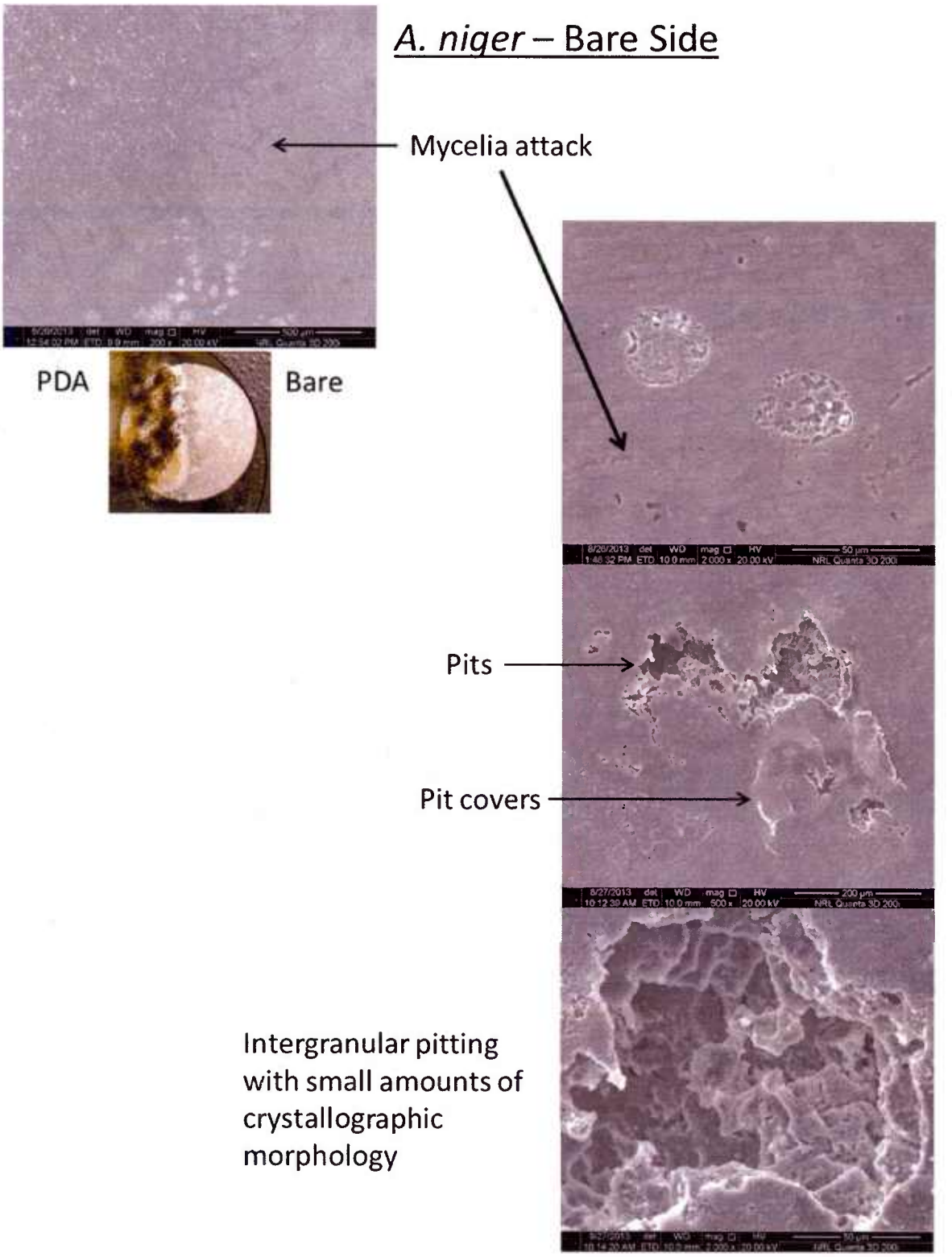

Figure 6. Bare AA5083-H116 coupons adjacent to PDA overlay after 90-day exposure in marine atmosphere with *A. niger*.

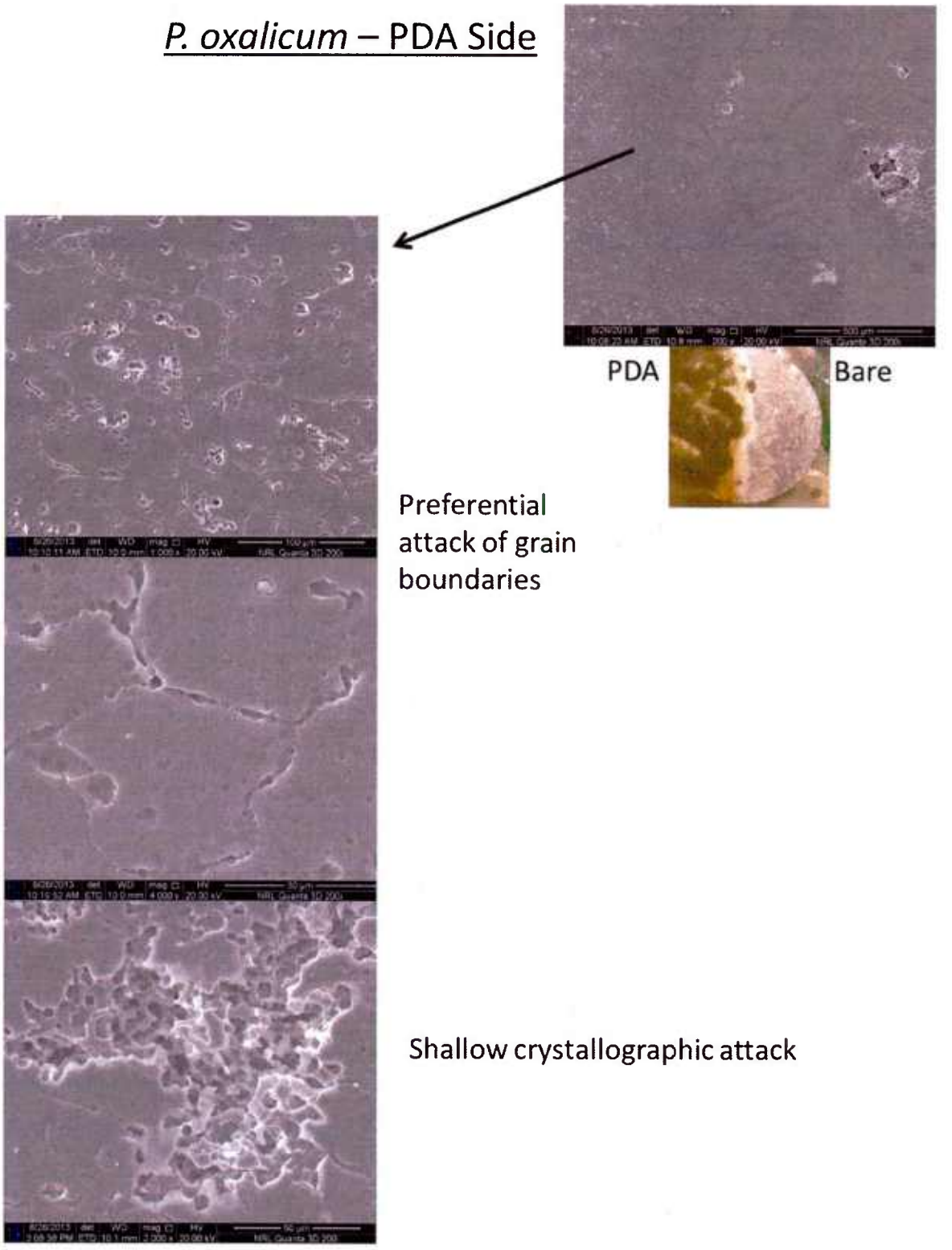

Figure 7. AA5083-H116 surface under PDA after 90-day exposure in marine atmosphere with *P. oxalicum*.

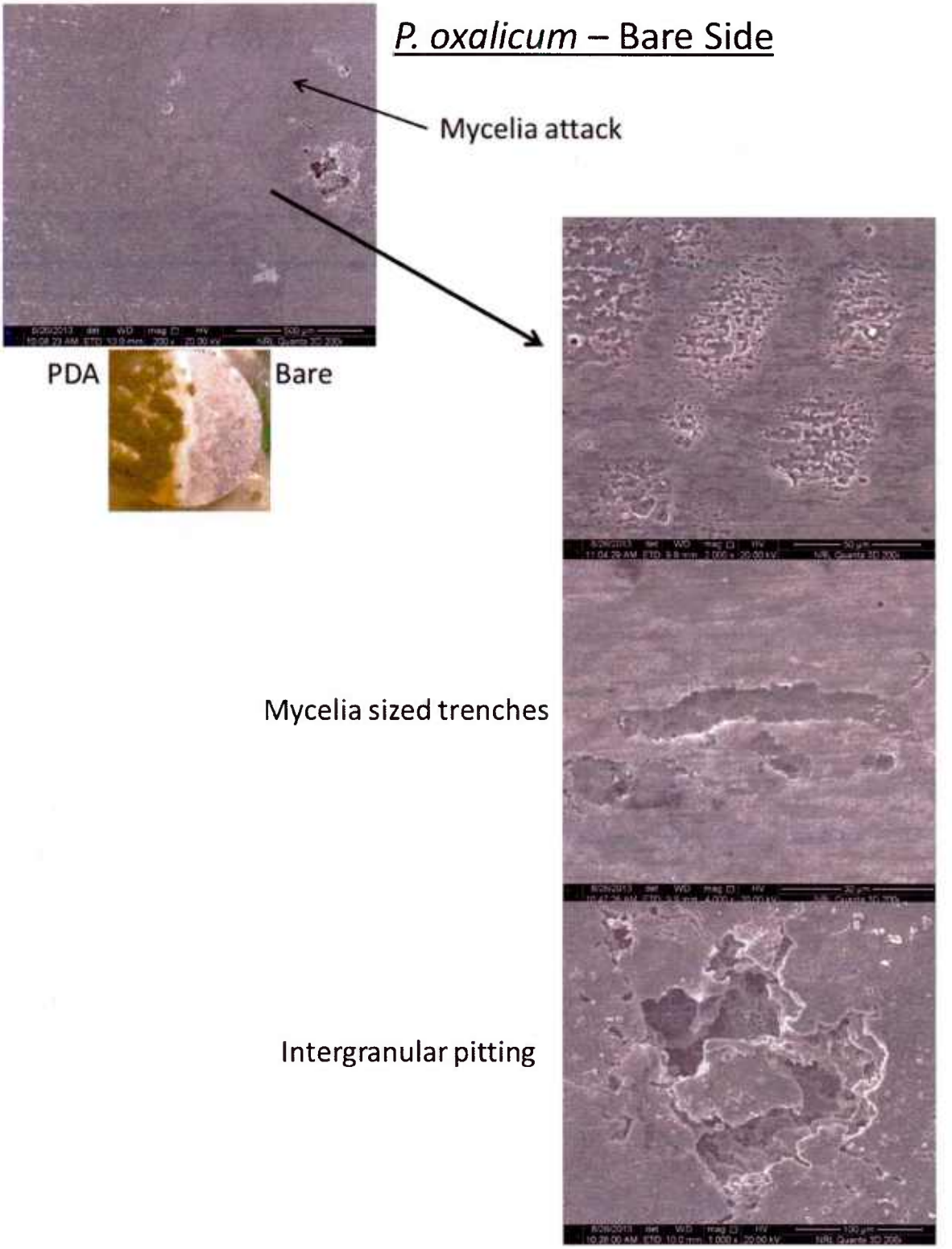

Figure 8. Bare AA5083-H116 coupons adjacent to PDA overlay after 90-day exposure in marine atmosphere with *P. oxalicum*.